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Structuring peculiarities of polytetrafluoroethylene modified with boron nitride when activated with ultrasonic exposure

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Abstract

High reliability and durability of metal-polymer friction units widely used in petrochemical process equipment is inextricably connected with the use of new materials with advanced serviceability. The paper presents the influence patterns of ultrasonic exposure on the structural features of the synthesized polymer composite material based on polytetrafluoroethylene, modified with boron nitride, that results in the supramolecular structure change, the crystallinity degree increase and the matrix blocks growth. Ultrasonic activation of polytetrafluoroethylene modified with boron nitride leads to the wear rate and friction coefficient decrease.

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Keywords: polytetrafluoroethylene; friction units; modification; ultrasound; composite synthesis; structure; wear

1. Introduction

Maintenance of high reliability and durability of metal-polymer friction units widely used in petrochemical machinery and process equipment is inextricably linked with the use of new materials possessing the appropriate physico-mechanical properties. Sealing devices, bearings, thrusts made of such materials can significantly increase the life of a machine as a whole [1-4].

In this regard polytetrafluoroethylene (PTFE) has the preferred complex of parameters as they predetermine its widespread use as structural materials. Necessity of more stringent requirements for the reliability of structural components stimulates development of new generation materials on the basis of PTFE [5–7].

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The most promising method of significant improvement of PTFE exploitation parameters is a transition to based on it composites. Modern techniques of enhancing the mechanical properties of polymeric materials predict a solution to this problem in frames of a polymer nanocomposites model [8]. Hexagonal boron nitride has great prospects being used as modifying filler [9, 10].

At the same time, it is difficult to obtain high-quality products from PCM which is modified with boron nitride. The situation may be changed with energy influence on the composition mixture with its ultrasonic activation. As the effect of ultrasonic vibrations (USV) energy on the structure and properties of polytetrafluoroethylene modified with hexagonal boron nitride is not yet fully examined, researches in this area are very promising [11].

2. Study subject

The study subject is disperse filled polytetrafluoroethylene modified with hexagonal boron nitride powder (Table 1).

Table 1. Boron nitride concentration in polytetrafluoroethylene.

Sample №	Boron nitride concentration (NB), %
1	1.0
2	3.0
3	5.0
4	10.0

Samples for research were obtained with charge pressing technology consisting of powdered polytetrafluoroethylene with a filler with fineness of 50-100 microns, mixed in a mill with blades speed 7800 min^{-1}. Special experimental test-bench based on hydraulic press was used to manufacture samples [12]. The test-bench allows making samples with two different pressing parameters - both with the activation of composite mixture with external ultrasound exposure and without it. After pressing the samples were subjected to heat treatment (sintering) at a temperature of 360^o C.

3. Methods

Study of PCM supramolecular structure was carried out with X-ray diffraction analysis method on the X-ray powder diffraction apparatus D8 Advance (Bruker) in Cu-kα radiation (wavelength is 0.15406 nm) using a position-sensitive detector Lynxeye.

The following measurement modes are used:

1. for phase analysis: scan step is 0.05º, time of signal accumulation is 2 sec/point, div.slit=0.5, voltage and filament current are 40 kV and 40 mA, respectively; scan area is 2θ: 5-100^o (for "Boron nitride" samples); 5-80^o (for PTFE).
2. to calculate the lattice parameters and size of crystal lattice: scan step is 0.02^0, time of signal accumulation is 2 sec/point, div.slit=0.3, voltage and filament current are 40 kV and 40 mA, respectively; scan area is 2θ: 5-80^o; the sample was added with silicon powder Si (SRM 640d) as the internal standard.

Interpreting of obtained X-ray diffraction patterns was performed using data base on powder diffraction ICDD PDF-2, of 2006 year in the programme EVA (Bruker).

Research methodology of examined PCM tribological properties provided a comprehensive study of their durability (ware rate) and anti-friction properties (coefficient of friction). The research of materials wear resistance and anti-friction properties and their comparative assessment was carried out on a specially designed stand [13], sliding velocity was V=0.75 m/s at pressure P=2 MPa without lubricants.

Identification of ultrasonic energy influence laws on the structural features on synthesized polymeric composite material on the basis of the polytetrafluoroethylene modified with boron nitride is a very urgent task.

4. Results and discussion

Research of composite materials was carried out with study of the supramolecular structure and phase composition of the obtained materials by X-ray diffraction analysis (XRD). By analyzing the X-ray diffraction patterns one can get information about the molecular structure of the composite.

Interpretation of PTFE phase composition sample showed that it was homogeneous object which contains the PTFE phases (Fig. 1). PTFE X-ray diffraction patterns are characterized with an intense peak at d/n = 4.90 A (18.01° 2θ) of the crystalline phase and a series of low-intensity peaks, as well as two amorphous halo in 30-50° (2θ).

The presence of halo on PTFE X-ray diffraction patterns is associated with specific forms of macromolecules disorder different in the topology from amorphous and crystalline phases in other polymers.

The slight intensity ratio of the main peak and a halo that proves big topological disorder in the examined sample should also be noted.

The X-ray diffraction patterns of the examined samples regardless the mode of compressing; reflect amorphous-crystalline structure of boron nitride and PTFE mixtures with a degree of crystallinity (30-42%). This diffraction reflections of the crystalline part of polymers are at constant angles 2θ indicating the immutability of the phase composition at ultrasonic exposure.

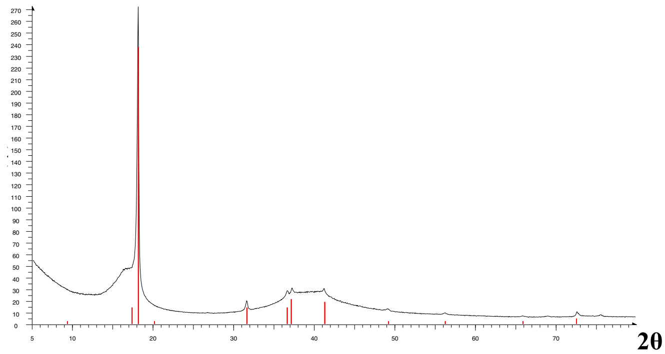

Fig. 1. Phase composition of PTFE sample.

X-ray diffraction patterns of samples № 1-4, representing a mechanical mixture of PTFE and boron nitride are composed of reflections characteristic for these compounds: intense reflex of the crystalline phase in the area 18° and 27°; a set of narrow peaks at large angles values; "powerful" amorphous halo with 32~44° **2θ.** Typical X-ray diffraction patterns of the modified PTFE obtained by the examined technologies are shown in Fig.2 and 3. The ratio of reflexes intensities corresponds to the component concentration.

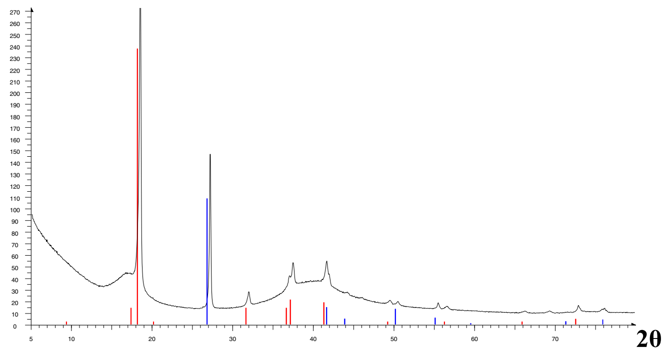

Fig. 2. Phase composition of sample № 1 without ultrasonic exposure.

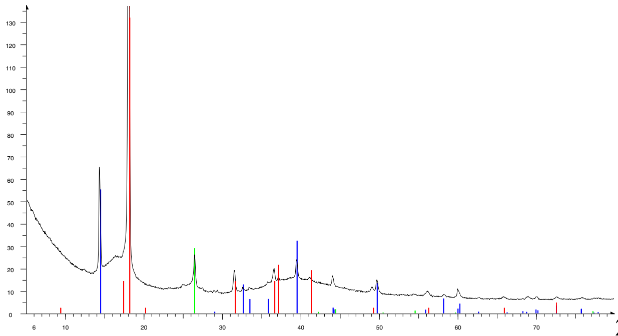

Fig. 3. Phase composition of sample № 1 with ultrasonic exposure.

Computer analysis (Crystallographica Search-Match Version 3.1.0.0) recognizes these reflexes as belonging to NB phase. The intensity of NB reflexes at all angles is substantially lower than PTFE peak (2θ = 18.00°) for all the samples. These peaks indicate the presence of other structural phases, and they are common to all the samples. To determine the composition of these structures special study is required.

Basic reflexes of fluoropolymer indicate the presence of phases with different macromolecular fluorocarbon chains conformation. Relations of interplanar spacing squares in the first, second and third crystalline reflexes indicate hexagonal structure of the crystalline phase. The XRD patterns of the samples differ from the diffraction patterns of the fluoropolymer starting material with absence of reflexes that characterize disorder of C_2F-groups on the hexagonal axis of the crystal phase exhibited in the rotational disorientation and chain molecules shift relative to each other.

PTFE has low polymeric fractions and high polymeric fractions, the first form the mesostructure forming a halo (32-44°) in the observed diffraction patterns.

Additional processing of the X-ray diffraction patterns of the examined composites samples was carried out to extract information about the characteristics of the supramolecular structure: permanent hexagonal crystal cells a_{cr} and C_{cr}, crystallite size in the direction of [100], the crystallinity degree.

The calculated values of microstructural characteristics and the relative degree of composites crystallinity are shown in Table 2.

Table 2. Characteristics of the supramolecular structure of the examined composites.

Sample labeling	CK, %	a_{cr}, nm	Ccr, nm	D, nm
№ 1 without ultrasound	30	0.5693	1.588	33.4
№ 1 with ultrasound	36	0.5681	1.579	38.5
№ 2 without ultrasound c	31	0.5689	1.584	34.4
№ 2 with ultrasound	36	0.5681	1.579	38.5
№ 3 without ultrasound c	31	0.5673	1.591	43.1
№ 3 with ultrasound	42	0.5670	1.570	43.2
№ 4 without ultrasound	40	5.563	15.48	36.4
№ 4 with ultrasound	41	5.566	15.58	36.6

The greatest change of the supramolecular structure is found to take place in the samples with 5% concentration of hexagonal boron nitride (Sample № 3). At the same time, the degree of crystallinity increases significantly to 42%. The data of X-ray diffraction analysis obtained for samples subjected to ultrasonic exposure, showed that the degree of crystallinity in processing also increases and the most significant result is for the samples with 5% NB (from 31 to 42%). This result is a direct indication of the supramolecular structure reorganization.

At the same time, for low NB concentrations crystalline hexagonal cell constants a_{cr} and C_{cr} are reduced due to PCM ultrasonic processing and the crystallite size in [100] direction increases. In case of higher NB concentration (10 wt.%) ultrasonic exposure practically has no effect on the crystal hexagonal cell parameters and crystallite size, and the degree of crystallinity increases slightly.

The nature of changes in the degree of crystallinity according to fillers content shows lack of influence uniqueness on PTFE crystallization processes. Increasing the degree of crystallinity with increasing filler content is most likely due to the increase in the crystallite size. It creates perfect supramolecular structure characterized with formation of small spherulites of the same geometrical shapes and sizes, even their distribution in the matrix volume corresponding to the best deformation-strength parameters of the material and contributing to reduce the composites wear due to the increased proportion of fillers structural active surface, crystallization processes take place on it.

Changing the properties of crystalline polymers with the fillers introduction is determined primarily with changes in the amorphous phases. In filled crystallizing polymer the filler can contribute the crystalline phase into more equilibrium state and amorphous state into less equilibrium. Since the filler has a tendency for accumulating in less ordered areas, the effect of the filler on the properties of crystallizing polymer related to its effect on the amorphous part can be achieved at much lower filler content than when introducing it into amorphous polymer. It may also be one of the reasons for increasing the strength characteristics of the filled crystalline polymers at low filler concentrations. This composite behavior indicates an increase in the interaction of the filler particles to the polymer matrix as a result of ultrasonic processing.

The results of tribological tests are shown in Fig. 4, 5.

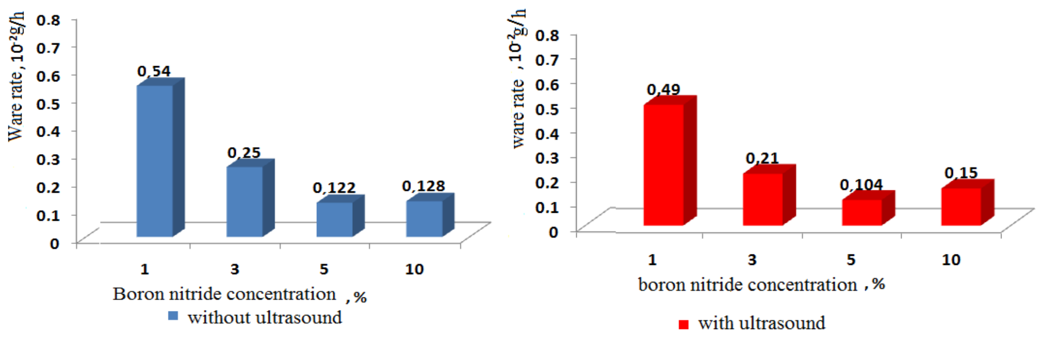

Fig. 4. The wear rate dependence on concentration of boron nitride.

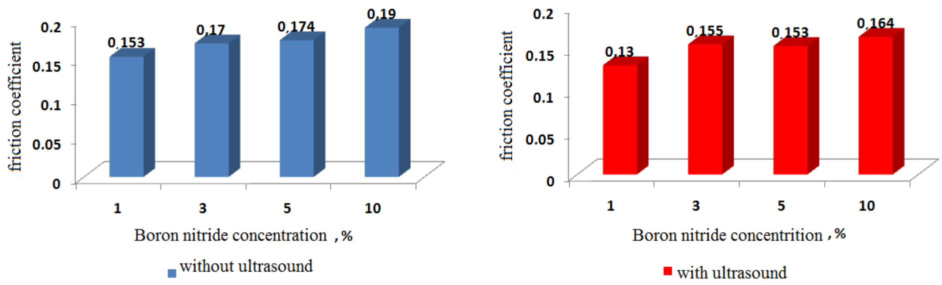

Fig. 5. The dependence of the friction coefficient on the concentration of boron nitride.

Analyzing the results, it can be noted that the activation of the compositional mixture throughout the concentration range h-NB leads to reduce of wear rate up to $0.104 \cdot 10^{-3}$ g/h at rational filler concentration of 5 %, which is 17 % less than that of a composite obtained with extrusion without imposing ultrasonic vibrations. At the same time composite mixture activating results in reduction of the friction coefficient from 0.174 to 0.153 at rational filler concentration of 5 % in comparison with the PTFE mixture synthesized without activating with ultrasonic vibrations that is 13.7 %.

The reason for reducing the wear rate and coefficient of friction of composites of boron nitride may be the increase in mobility of the molecular chains of the polymer matrix in a thin surface layer and more favorable redistribution of stresses at frictional contact, and a friction pair is lubricated due to boron nitride presence in the composite matrix. Due to higher sorption capacity of boron nitride to hydrocarbons its particles are capable of keeping the shell from the adsorbed molecules of lubrication components and deliver them to the friction zone where there is their depletion in tribo-contact zone when the temperature rises. Thus, there is an adhesive wear prevention of the rubbing surfaces.

5. Conclusion

We state that the combined influence of ultrasonic exposure of the NB filler particles leads to significant changes in the supramolecular structure of composite material based on polytetrafluoroethylene and expressed in an increase of crystallinity degree and the block size in the crystalline phase structure.

The best tribological properties of polytetrafluoroethylene take place in its modification with 5% boron nitride. Activating of such composite material with ultrasonic exposure reduces wear rate to 17% and the friction coefficient to 13.7%

The results can be used for the manufacture of non-lubricated and lubricated metallopolymer friction pairs of compressors and pumps at such enterprises as the SPE "Sibcriotechnika" and JSC "Gazpromneft-Omsk Refinery".

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